FORM PTO-1390 (REV 11-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE ATTORNEY'S DOCKET NUMBER 57.0291 US PCT TRANSMITTAL LETTER TO THE UNITED STATE DESIGNATED/ELECTED OFFICE (DO/EO/US U.S. APPLICATION NO. (If known, see 37 CFR 1.5 622454 CONCERNING A FILING UNDER 35 U.S.C. 371 INTERNATIONAL APPLICATION NO INTERNATIONAL FILING DATE PRIORITY DATE CLAIMED PCT/GB99/00298 28 January 1999 17 February 1998 TITLE OF INVENTION Anti-accretion additives for drilling fluids APPLICANT(S) FOR DO/EO/US Louise Bailey and Boyd Grover Applicant herewith submits to the United States Designated/Elected Office (DO/FO/US) the following items and other information This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371 This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C.371(b) and PCT Articles 22 and 39(1) A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. A copy of the International Application as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (required only if not transmitted by the International Bureau). has been transmitted by the International Bureau. is not required, as the application was filed in the United States Receiving Ofice (RO/US). A translation of the International Application into English (35 U.S.C. 371(c)(2). Amendments to the claims of the International Application under PCT Article 19(35 U.S.C. 371(c)(3)) are transmitted herewith (required only if not transmitted by the International Bureau). have been transmitted by the International Bureau. have not been made; however, the time limit for making such amendments has NOT expired. have not been made and will not be made. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 71(c)(3)). An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11, to 16, below concern document(s) or information included: An Information Disclosure Statement under 37 CFR 1.97 and 1.98. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. 1 A FIRST preliminary amendment. A SECOND or SUBSEQUENT preliminary amendment. A substitute specification. A change of power of attorney and/or address letter. 16. Other items or information:

534 Rec'd PCT/P:0 15 AUG 2000 -

Carlo
4
(iii
N
2.45
100
品 医
100
ž
- far
-
-
100
Sept.

U.S. APPLICATION OF THE	622454	INTERNATIONAL APPLICATION NO PCT/GB99/00	298	57,0291 US P	
17 X The fall	owing feet are submitt			CALCULATIONS	
17. X The following fees are submitted BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):					
		nination fee (37 CFR 1.482)			
		1.445(a)(2)) paid to USPTO epared by the EPO or JPO · · · ·	\$970.00		
International p USPTO but In	preliminary examination sternational Search Reno	fee (37 CFR 1.482) not paid to ort prepared by the EPO or JPO.	\$840.00		
		fee (37 CFR 1.482) not paid to US IS(a)(2)) paid to USPTO	SPTO but		
International	preliminary examination	n fee paid to USPTO (37 CFR 1.4 ns of PCT Article 33(1)-(4	182) \$670.00		
International	preliminary examination	n fee paid to USPTO (37 CFR 1.4 PCT Article 33(1)-(4)	182)		_
	ENTER APPR	OPRIATE BASIC FEE AN	MOUNT =	\$ 840.00	
		ath or declaration later than 2 date (37 CFR 1.492(e)).	20 30	\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	17 - 20		X \$18.00	s -	
Independent claims	2 -3		X \$78.00	s -	
MULTIPLE DEP	ENDENT CLAIM(S) (if a		+ \$260.00	\$	
		L OF ABOVE CALCULA		\$ 840.00	
	for filing by small entit I (Note 37 CFR 1.9, 1.2	y, if applicable. A Small Entity S 7, 1.28).	tatment	\$	
		SUB	TOTAL =	\$	
Processing fee of months from the	\$130.00 for furnishing earliest claimed priority	the English translation later than date (37 CFR 1.492(f)).	20 30	s	
TOTAL NATIONAL FEE =			IAL FEE =	s 840.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment mus be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property			\$		
TOTAL FEES ENCLOSED =			\$ 840.00		
				Amount to be:	s
1				charged	s
a. A checi	Linda	to cover the abo	6 !		
a. L. A chec	k in the amount of	to cover the abo	ve rees is encrose	a.	
	charge my Deposit Acco		amount of \$_84	10.00 to co	ver the above fees.
c. The Co	mmissioner is hereby au	thorized to charge any additional	fees which may b	e required, or credit	any
overpay	overpayment to Deposit Account No. 04:1579 . A duplicate copy of this sheet is enclosed.				
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR				vive (37 CFR	
1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRE	SPONDENCE TO:		1610	CRU /1 //Sca	ZM)
	ger Technology Corp	oration	SIGNATU	JRE:	m -
	berger Drive, MD1		Gordo	on Waggett	
Sugar Land TX 77478 USA			NAME		
1			34,47	6	
			REGISTR	ATION NUMBER	

ATTORNEY DOCKET NO. 57.0291 EXPRESS MAIL NO. EK802769773US

534 Rec'd PCT/PTO 16 AUG 2000

"EXPRESS MAIL" MAILING LABEL

NUMBER: DATE OF DEPOSIT: DATE OF DEPOSIT: (Lugust 16, 2000)

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICES "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED ABOVE AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

Tricia Van Hooser (typed or printed name of person mailing paper or fee)

**Thecka & Tan Hoose
(signature of person mailing paper or fee)

UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

In re Application of:)	Attorney Docket No: 57.0291
Louise Bailey)	
Boyd Grover)	
)	
)	
Serial No.: Unknown)	Group Art Unit: Unknown
)	
Filed: Herewith)	
)	
For: ANTI-ACCRETION ADDITIVES)	Examiner: Unknown
FOR DRILLING FLUIDS)	
)	
)	

PRELIMINARY AMENDMENT

Box PCT Assistant Commissioner for Patents Washington, D.C. 20231

Sir

Prior to calculating the fee due for the above-identified application and prior to the first Office Action, please amend the above-identified application, as follows:

IN THE CLAIMS

Before claim 1, insert -- What is claimed is: --

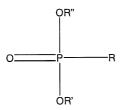
Please cancel claims 1-8.

Please amend the following claims:

In claim 15, before "of preventing accretion", delete "Method" and insert -- A method--.

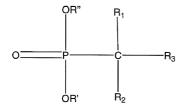
Please add the following claims:

Claim 17. A drilling fluid being water-based and having an inhibitive component to reduce the hydration of shale further comprising an additive in accordance with the formula



where R, R' and R" are groups of non-polymeric character.

Claim 18. The drilling fluid of claim 17, comprising an additive in accordance with the formula



where R1, R2 and R3 are groups of non-polymeric character.

Claim 19. The drilling fluid of claim 17, wherein the additive is based on a phosphor derivative of the succinic acid.

Claim 20. The drilling fluid of claim 17, wherein the additive is based on a short chain phosphorylated hydrocarbon.

Claim 21. The drilling fluid of claim 17, comprising the additive in a concentration of up to about 10% weight by volume.

Claim 22. The drilling fluid of claim 17, being a reactive anionic drilling fluid.

Claim 23. The drilling fluid of claim 17, being a phosphate-based drilling fluid.

Claim 24. The drilling fluid of claim 21, being a silicate-based drilling fluid.

Claim 25. A method of preventing accretion of cuttings in a borehole, said method comprising the step of using a drilling fluid in accordance with claim 17 during a drilling operation.

REMARKS

The above amendments do not add any new matter. Favorable consideration of this application is requested. Please do not hesitate to contact the undersigned by phone for prompt resolution of any outstanding issues. It is believed that no fee is due for this Preliminary Amendment, however, if such a fee is due, the Commissioner is authorized to charge such fee, or credit overpayment, to Deposit Account No. 04-1579(57.0291).

Respectfully submitted.

Gordon G. W.

Reg. No.: 34,476 Attorney for Applicant(s)

Date: 16 August 00

Schlumberger Technology Corporation 110 Schlumberger Drive, MD1 Sugar Land, Texas 77478 Ph: (281) 285-8606

Fax: (281) 285-8569

WO 99/42539

402 Rec'd PCT/FT0 16 AUG 2000

Anti-accretion additives for drilling fluids

This invention relates to anti-accretion additives for drilling 5 muds.

BACKGROUND OF THE INVENTION

Bit-balling and cuttings accretion are problems encountered when

drilling shales, particularly with water-based muds. Shale
cuttings can adhere to each other and to the bottom hole
assembly and cutting surfaces of the bit. Gradually a large
plastic mass builds up which can block mud circulation and
reduce rates of penetration. There is a "danger zone" of clay

plasticity for balling and accretion, related to the water
content of the clay or shale, which can be defined in terms of
the Atterberg limits of soil mechanics. In the dry zone the clay
has too little water to stick together and it is a friable and
brittle solid. In the wet zone the material is essentially

liquid like with very little inherent strength and can be washed
away.- Intermediate to these zones, i.e., in the danger zone,
the shale is a sticky plastic solid with greatly increased
agglomeration properties and inherent strength.

25 When cuttings are exposed to conventional water-based muds they usually imbibe water and pass rapidly through these different zones, eventually dispersing. However recent advances in drilling fluid technology have developed highly inhibitive muds which appear to reduce the hydration of shale and in doing so
30 maintain the cuttings in the danger or plastic zone contributing to increased accretion and bit-balling. Field experiences with glycol, phosphate and silicate muds in particular have shown accretion problems.

10

WO 99/42539 PCT/GB99/00298

- 2 -

US patent 5,639,715 describes additives for bit-balling prevention based on sulphonosuccinate chemistry.

Phosphorus based additives and compound have been used in the oilfield industry mainly for the purpose of enhancing oil recovery from production wells.

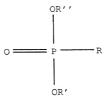
It is the object of the present invention to find alternatives to the known methods of preventing accretion.

SUMMARY OF THE INVENTION

The invention is an additive for drilling mud. The additive

15 reduces the accretion and bit-balling tendencies of cuttings
exposed to said muds. The additives are based on phosphonate
chemistry, and are preferably of the general class:

(I)



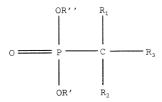
20

wherein R, R' and R' are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

25 In a more preferred embodiment, the additives are based on the formula

10

(II)



wherein R_1 , R_2 and R_3 are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

In a preferred embodiment of the invention, the additives are containing not more than one phosphor atom.

In another preferred embodiment of the invention, the additive is a phosphor derivative of the succinic acid or short chain phosphorylated hydrocarbons.

15 Additives according to the invention are added to the drilling fluid at levels 0.1-10%, preferably 1-5%, weight by volume (%kg/liter). The drilling fluid itself may be oil based, though it is recognized that accretion tends to be less pronounced in drilling muds of this kind. Therefore, the preferred drilling fluid in accordance with the present invention is water based, even more preferably a reactive anionic based drilling fluid, such as silicate or phosphate based muds. Further additives as known in the art may be added to impart other desired properties to the mud system. Such known additives include viscosifying

25 agents, filtrate reducing agenst, and weight adjusting agents. Other preferred additives are shale-swelling inhibitors, such as salts glycol-, silicate- or phosphate-based agents, or any combination thereof. - 4 -

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description below.

MODE(S) FOR CARRYING OUT THE INVENTION

A test used to determine the anti-accretion properties of additives involves squeezing shale or clay cuttings between two steel plates with a given force causing them to stick to each other and the plates. The force required to slide the plates apart is then determined using a force gauge or spring balance.

Oxford clay cuttings of size 2-4mm were soaked in the test fluid 15 for 15 minutes. The excess mud was drained from the cuttings using a sieve (500 micron mesh). A small pile of cuttings (5-10g) was put onto the base plate of the tester. The pile was roughly levelled and the top plate replaced over the cuttings. A PTFE spacer was placed on top of the top plate. A screw-mounted 20 plunger in the tester housing was wound down until it made contact with the spacer. A torque wrench was used to tighten the plunger onto the top plate. The standard torque was 75 inchpounds (~9N.m). Immediately on reaching this value, the plunger was wound back sufficiently to remove the spacer. A force gauge 25 or spring balance was then connected to the top plate. The tension on the top plate was then increased by pulling on the force gauge until the plate breaks free from the cuttings bed. The maximum force recorded was the freeing force for the plate or accretion value. Values can range from 1.0 to above 20.0 kg 30 force.

The phosphonate based additives tested in accordance with the above procedure are added to a water-based mud containing tetrapotassium pyrophosphate (TKPP) and consisting of

35

1000 ml fresh water (base)

5

- 85.5 g tetrapotassium pyrophosphate (shale inhibitor)
- 2.85 g xanthan gum (viscosifier)
- 11.4 g carboxy methyl cellulose of low viscosity grade
 (filtrate reducer)
- 5 42.75 g simulated drill solids
 barite (weighting agent) to density 1.08 sg .
 NaOH to pH 9.2
 biocide
 - 10 Baseline accretion values were established as:

Simple polymer mud 5 kg TKPP mud 21.7 kg

15 The anti-accretion additives were then added to the TKPP mud at levels of 1-5%.

Additives which reduced the accretion value from $>10\,$ kg to 9 kg or below were:

- 20
- Hydrolysed polymaleic acid
- 3-phosphonopropionic acid
- succinic acid
- propyl phosphonic acid
- 25 dibutyl-butyl phosphonate
 - hydroxyphosphonoacetic acid
 - dimethylpropyl phosphonate
 - phosphorous acid
 - diethyl-ethylphosphonate
- 30 ethylmethacylate phosphate
 - tri-ethyl phosphonoacetate
 - tetramethyl phosphonosuccinate
 - phosphonosuccinic acid
 - 2-hydroxyethyl phosphonic acid.

The last five additives (Additives 9-14) were the found most effective. For those the following values were recorded:

TKPP mud + (%)additive:	Accretion value
1% diethyl-ethylphosphonate	8 kg
5% diethyl-ethylphosphonate	7 kg
5% ethylmethacrylate phosphate	6 kg
1% tri-ethyl phosphonoacetate	8 kg
5% tri-ethyl phosphonoacetate	5 kg
5% tetramethyl phosphonosuccinate	7 kg
5% phosphonosuccinic acid	7 kg
5% 2-hydroxyethyl phosphonic acid.	. 7 kg

15

5

10

In a second series of tests with the additives, silicate mud of the following composition was used:

1000 ml sea water (base)

20 131 g Na silicate, a solution of 14% NaOH and 27% SiO_{2 (shale inhibitor)}

117.5 g KCl (shale inhibitor, weighting agent)

20 g Polyanionic cellulose (filtrate reducer)

5 g Xanthan gum (viscosifier)

25 NaOH to adjust pH to 12.

Baseline accretion values were established as:

simple polymer mud 9.5 kg 30 silicate mud 17.7 kg

The anti-accretion additives were tested in the silicate mud at 1% (w/v):

	Silicate mud + (1%)additive:	Accretion value
	diethyl-ethylphosphonate	11.1 kg
	tri-ethyl phosphonoacetate	11.35 kg
5	tetramethyl phosphonosuccinate	9.96 kg
	phosphonosuccinic acid	10.8 kg
	2-hydroxyethyl phosphonic acid	11.4 kg

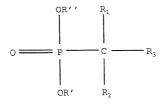
In most cases the accretion value has been reduced 10 significantly, down to the levels of a simple polymer mud. Additive for a drilling fluid, consisting of a compound in accordance with the formula

OR''

wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of $100~{\rm atoms}$.

 The additive of claim 1, wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C or O.

 The additive of claim 1, consisting of a compound in accordance with the formula



wherein R_1 , R_2 and R_3 are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

10

15

5

- 4. The additive of claim 3, wherein $R_1,\ R_2$ and R_3 are radicals exclusively containing H atoms or combinations of H, C or O.
- 5 5. The additive of claim 1, based on a phosphor derivative of the succinic acid.
 - The additive of claim 1, based on a short chain phosphorylated hydrocarbon.

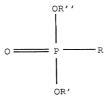
10

15

20

- Drilling fluid comprising an additive in accordance with claim 1.
- 8. The drilling fluid of claim 5, comprising an additive in accordance with claim 1 in a concentration of up to about 10% weight by volume.
- A drilling fluid comprising water as base component;
 - a viscosifying agent to increase the viscosity of the fluid; a filtrate reducing agent;
 - a weighting agent to adjust the density of the fluid; and an additive for a drilling fluid, consisting of a compound in accordance with the formula

25

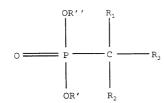


wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

10. The drilling fluid of claim 9, wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C or O.

5

11. The drilling fluid of claim 9, wherein the additive consists of a compound in accordance with the formula



10

wherein R1, R2 and R3 are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

15

12. The drilling fluid of claim 11, wherein R_1 , R_2 and R_3 are radicals exclusively containing H atoms or combinations of H, c or o.

20 13. The drilling fluid of claim 9, further comprising a shale swelling inhibition agent.

25

14. The drilling fluid of claim 13, wherein the shale swelling inhibition agent comprises phosphate- or silicate-based compounds.

15. Method of preventing accretion of cuttings in a borehole, said method comprising the step of adding to a drilling fluid an additive in accordance with claim 1 prior to or during a drilling operation.

16. The method of claim 15, wherein the additive is added in a concentration of up to about 10% weight by volume of the drilling fluid.

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DECLARATION FOR PATENT APPLICATION

Declaration Submitted WITH Initial	Filing	OR	Declaration Submitted After Initial Filing
Attorney Docket Number: First-Named Inventor:			57.0291 Louise Bailey
Application Number: Filing Date: Group Art Unit: Examiner's Name:	COMPLETE IF KN		OWN: 09/622,454 August 16, 2000
As a below-named inventor, I hereby	declare that:		
My residence, post office address and	d citizenship ar	e as sta	ated below next to my name.
inventor (if plural names are listed below) of the invention entitled:	he subject matt	er whic	one name is listed below) or an original, first and joint ch is claimed and for which a patent is sought on the DRILLING FLUIDS
the specification of which:			
is attached hereto as Attorney Docket No.:	57.0291		
OR			
□ was filed on August 16, 2000 □ PCT International Application No □ and was amended on	MMDDYY).	Jnited S	States Application No. 09/622,454 or
I hereby state that I have reviewed at the claims, as amended by any amendment refer		the cont	tents of the above identified specification, including
Lacknowledge the duty to disclose in	formation which	ch is ma	aterial to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 1.19(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of

the application on which priority is claimed:

DSSCRAME ILLEGO

Prior Foreign	Country	Foreign Filing Date	Priority Not	Certified	Copy Attached?
Application Numbers		(MMDDYY)	Claimed	Yes	No
PCT/GB99/00298	wo	JAN 28, 1999			\boxtimes
9803249.3	GB	FEB 17, 1998			⊠

Additional foreign application numbers are listed in a supplemental priority data sheet PTO/SB/02B, attached hereto.

39,871

Douglas Y'Barbo

. I hereby claim the benefit under Title 35 U.S.C. § 1.19(e) of any United States provisional application(s) listed below.						
	Application Numb	er Filing	Date			
Additional provisi attached hereto.	onal patent application numbers	s are listed in a suppleme	ental priority data sheet PTO/SB/02B,			
I hereby claim the benefit under 35 U.S.C. § 1.20 of any United States application(s), or § 365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph 35 of U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentiability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.						
US Parent Application Number	PCT Parent Number	Parent Filing Date (MMDDYY)	Parent Patent Number (if applicable)			
☐ Additional US or PCT international application numbers are listed in a supplemental priority data sheet PTO/SB/02B, attached hereto. As a named inventor, I hereby appoint the following attorney(s) and/or agents(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:						
Name	Registration Number	Name	Registration Number			
Maryam Bani-Jamali	36.084					
Gordon G. Waggett						
	34,476	Victor Segura	44,329			
-Robin C. Nava	42,926	J. H. Bouchard	29,286.			
Robin C. Nava John J. Ryberg	42,926 31,134	J. H. Bouchard Wayne I. Kanak	29,286 35,564			
-Robin C. Nava	42,926	J. H. Bouchard	29,286.			

☐ Additional registered practitioner(s) named on supplemental Registered Practitioner Information Sheet PTO/SB/02B, attached hereto.

I hereby direct that all correspondence and telephone calls be addressed to:

 Name
 Maryam-Bani-Jamali

 Address
 Schlumberger Technology.Corporation

 Address
 110 Schlumberger Drive_MD1

 City
 Sugar Land
 State
 Texas

 City
 Sugar Land
 State
 Texas
 Zip
 77478

 Country
 U.S.A.
 Telephone
 28T-285-4524
 Fax
 281-285-8569

William L. Wang

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the

United States Code and that such willful false statements may jeopardize the validity of the application or any patent

issued thereon.				
Sole or first inventor: Inventor's Full Name	Louise (First)	(Initial)		Bailey (Last)
) Inventor's Signature:	Louise Bailey	1	Date: 3 ·	9 . 00
Residence Street Address	58 The High Street, Yelling, St. N	leots, Cambridges	hire PE19 4SO	United Kingdom
Country of Residence:	UK	Citizenship:	PK	
Second inventor:	-			Grover
Inventor's Full Name	Boyd (First)	(Initial)		(Last)
Inventor's Signature:	Bull and	1	Date: 22	1000
Residence Street Address	12 Roslin Close, Harwood Park, I	Bromsgrove Wor	cestershire B60	2EZ. UK
Residence Street Address	12 Rosini Ciose, Hai wood I ark, I	Diomagiove, viol		J
Country of Residence:	UK	Citizenship:	UK (ef)	×